

UC Irvine

UC Irvine Previously Published Works

Title

The compatibility between aircraft and ground-based air quality measurements

Permalink

<https://escholarship.org/uc/item/7xm6r0jz>

Journal

Journal of Geophysical Research, 99(D1)

ISSN

0148-0227

Authors

Van Valin, Charles C
Boatman, Joe F
Luria, Menachem
[et al.](#)

Publication Date

1994-01-20

DOI

10.1029/93jd02679

Copyright Information

This work is made available under the terms of a Creative Commons Attribution License, available at <https://creativecommons.org/licenses/by/4.0/>

Peer reviewed

The compatibility between aircraft and ground-based air quality measurements

Charles C. Van Valin,¹ Joe F. Boatman,² Menachem Luria,^{1,2,3} Viney P. Aneja,⁴ Donald R. Blake,⁵ Michael Rodgers,⁶ and John T. Sigmon⁷

Abstract. Trace gas concentrations and atmospheric state parameters were measured aboard the NOAA King Air research aircraft during flights on August 16, 1988, along the Appalachian Mountains from central Pennsylvania to northern Georgia. Stepwise profiles were flown over five surface sites where measurements of certain atmospheric parameters were being made. A stationary cold front lying across southern Virginia effectively divided the area into two weather regimes; to the north of the frontal zone the air was slightly cooler and much drier than that to the south. Considerable convective activity developed from early to midafternoon along and south of the front. The comparison between the aircraft and ground sites included measurements of the primary pollutants SO₂ and several hydrocarbons, NO_y, the secondary pollutants H₂O₂ and O₃, and meteorological parameters. Continuity between the aircraft and surface meteorological and trace gas measurements was consistent at the northernmost site, which is situated in a relatively level valley. The agreement was poorer at the other four ground sites, which are located on or near mountaintops. Most of the meteorological and trace gas measurements, other than those made at Scotia, were found to differ by substantial margins, often by more than 10 times the resolution of the instruments. However, within a few hours after the flights, the surface measurements, particularly those of H₂O₂ and O₃, achieved values comparable to those measured with the aircraft, thus suggesting that air sampled at the canopy level did not mix readily with the bulk of the boundary layer.

1. Introduction

Since ground-level and aircraft measurements of meteorological parameters and atmospheric

trace gas concentrations are often used concurrently to understand the variability and distribution of the trace gases, it is essential to determine the comparability of these measurements. Although ground-level measuring sites can produce long-term continuous records of meteorological parameters and local concentrations of trace gases, the micrometeorology in the vicinity of a site influences the ability of measurements at the site to faithfully represent the wider atmospheric zone. On the other hand, instrumented aircraft can provide measurements over a wide area and thus provide three dimensional pictures of the distributions of the trace gases, and of the complementing meteorological parameters as well, but the length of the measurement record is limited to the aircraft flight time.

Although the literature contains many reports of O₃ or other trace gas measurements at ground locations, and numerous instances of measurements in the free atmosphere at various altitudes, there are relatively few comparisons of measurements aloft with ground-based measurements. In one such study, Harrison et al. [1978] compared tethered balloon-borne ozone-sonde measurements of O₃ at an English rural site, where surface measurements were also taken. Their results revealed that at times, such as during night-time inversions, there were significant changes in the O₃ concentrations within the first 50 m above the surface (e.g., from 15 to 60 ppbv). During times when the atmosphere was well-mixed no significant change was observed. In another study, Gotaas [1980] compared SO₂ and particulate sulfate data from numerous horizontal flights, grouped in altitude ranges, with those from ground stations located in the general vicinity of the flight paths. In general, the concentrations of both SO₂ and sulfate were similar to, but slightly lower than, the average of the aircraft observations taken below 500 m.

Two other important studies that were of more direct relevance to the present study were the Sulfate Regional Experiment (SURE) [Tommerdahl et al., 1981], and the Northeast Corridor Regional Modeling Project (NECRMP) [Possiel et al., 1984]. The SURE aircraft-ground comparisons, conducted during 1977 and 1978, showed that SO₂ and sulfate concentrations at the surface and within the mixed layer were significantly correlated. O₃ concentrations showed the "potential for being significantly correlated" during the afternoon, but not during the morning.

In the NECRMP study two situations were identified. In one group of cases, where the atmosphere was well mixed and the surface and aircraft O₃ measurements were not done on the

¹National Oceanic and Atmospheric Administration, Air Resources Laboratory, Aerosol Research Section, Boulder, Colorado.

²Cooperative Institute for Research in Environmental Sciences, University of Colorado, Boulder.

³Department of Environmental Sciences, The Hebrew University, Jerusalem, Israel.

⁴Department of Marine, Earth, and Atmospheric Sciences, North Carolina State University, Raleigh.

⁵Department of Chemistry, University of California, Irvine.

⁶School of Geophysical Sciences, Georgia Institute of Technology, Atlanta.

⁷School of the Environment, Duke University, Chapel Hill, North Carolina.

fringes of an urban plume, the average difference was 10 ppb, with the aircraft O_3 being greater than the surface two-thirds of the time. In contrast, in the other group of cases, when the atmosphere was poorly mixed, or when the measurement location was on the edge of an urban plume, the difference was large (averaging 49 ppb), with the higher O_3 concentration being almost always measured aloft.

In an attempt to compare aircraft and ground air quality measurements, four stepwise profile flights were flown with the NOAA King Air research aircraft over the NOAA Aeronomy Laboratory's Scotia, Pennsylvania, National Acid Precipitation Assessment Program field site on August 16, 21, 22, and 26, 1988, to gather air quality data for comparison with ground-based data. The findings were reported by Van Valin et al. [1991]. They demonstrated that the aircraft and ground atmospheric state parameter measurements at Scotia (wind speed and direction, temperature, and dew point) showed continuity from the surface to the aircraft observational altitude for all four flights. Secondary pollutant concentrations (H_2O_2 and O_3) were usually greater at the higher flight altitudes, but the lowest altitude measurements were in relatively good agreement with the surface measurements, and the indication of continuity to the surface was encouraging. The concentrations of SO_2 and NO_x agreed less well between aircraft and ground, exhibiting greater variability along the flight track. Their concentrations usually decreased with increasing altitude.

This paper compares measurements performed aboard the King Air and at ground sampling sites to determine if the results reported earlier are representative of other areas, and to extend the understanding regarding the compatibility of aircraft and ground-based atmospheric sampling. These measurements were made on two flights that took place on August 16, 1988, extending from the Scotia location as previously reported [Van Valin et al., 1991] to northern Georgia, including stepwise profiles over four additional ground-based atmospheric sampling sites.

2. Experimental Information

The Aerosol Research Section of NOAA's Air Resources Laboratory conducted two flights on August 16, 1988, with the NOAA King Air research aircraft, to compare ground-level and flight-level measurements at five locations in the Appalachian region. The first flight was from the Capitol City Airport (HAR), Harrisburg, Pennsylvania, to the Tri-Cities Airport (TRI) in northeastern Tennessee, and included stepwise profiles over the ground research stations at Scotia, Pennsylvania (SCO), operated by NOAA's Aeronomy Laboratory; at Shenandoah National Park, Virginia (SHN), operated by the University of Virginia; and at Whitetop Mountain, Virginia (WHT), operated by the Tennessee Valley Authority. The second flight was from northeastern Tennessee to northern Georgia; it then approximately retraced the flight path as far back as the airport at Roanoke, Virginia (ROA). Included in this flight were stepwise profiles over the Mt. Gibbs site in Mt. Mitchell State Park, North Carolina (MTM), operated by North Carolina State University; and the

Brasstown Bald, Georgia (BRB), site, operated by the Georgia Institute of Technology. The flight tracks, locations of the ground stations, and the times of the aircraft overflight are illustrated on a map of the eastern United States (Figure 1). Some geographic features in the vicinity of each of the surface sites, along with the flight tracks at the lowest altitudes above each of the sites, and at altitudes below the elevations of the WHT and MTM sites, are shown in Figure 2.

The instruments aboard the aircraft were described by Boatman et al. [1988, 1989]; calibration and preflight procedures, and instrument accuracy were described by Boatman et al. [1990] and Van Valin et al. [1991]. The continuous analyzers, from Thermo Environment Instruments, Inc., were the model 43S SO_2 analyzer, the model 49 O_3 analyzer, and the model 14B/E NO - NO_x analyzer modified to enhance sensitivity [Dickerson et al., 1984]. H_2O_2 was analyzed with the fluorescence analyzer described by Lazrus et al. [1986]. Gas analysis data reported from the ground sites were measured by similar instruments. Other continuous measurements included temperature, dew point, solar irradiance, and by means of the LORAN navigation system, position, heading, wind speed, and wind direction. Meteorological measurements at the ground sites were taken from 10-m towers, except at SHN, where the instruments were mounted at a height of 16.5 m, which is above the top of the forest canopy. Air intake heights for the trace gas continuous analyzers were 10 m, 3 m, 5 m, 5 m, and 5 m above ground at SCO, SHN, WHT, MTM, and BRB, respectively. Flask samples, later analyzed for C_2H_6 , C_2H_2 , C_3H_8 , and $n-C_4H_{10}$, were collected over each ground site at the lowest flight altitudes. Concurrently, two flask samples were collected at each ground site. Fabrication of the flasks and analysis of the samples were as described by Blake et al. [1992], and the analyses were done sequentially with the samples as reported there.

The meteorological instruments aboard the King Air are occasionally compared with and calibrated against the instruments mounted on the Boulder Atmospheric Observatory (BAO) tower; this was done prior to the start of the 1988 summer field research effort. The BAO is an instrumented 300-m tower 20 km east of Boulder, Colorado; elevation at the base of the tower is 1570 m. During the comparison-calibration flights, the aircraft flies directly over the tower, and past it at the 200- and 300-m levels to compare the pressure (altitude) and position by LORAN, and to calibrate the temperature measurements. The true air speed and heading measurements, which are made by independently calibrated instruments, are combined with the position indication from the LORAN, to provide, through first principles, the wind direction and wind velocity. The differences between the aircraft instrument readings and the BAO output were always within $\pm 1\%$ for temperature, dew point, and pressure. The uncertainty for wind speed and direction was found to be $< \pm 10\%$, or $\pm 0.5 \text{ m s}^{-1}$ for wind speeds less than 5 m s^{-1} .

Data from the aircraft continuous analyzers were averaged at both 10-s and 1-min intervals. The 1-min averages from the aircraft represent sampling distances of about 5 km. A nearly constant altitude was maintained for several

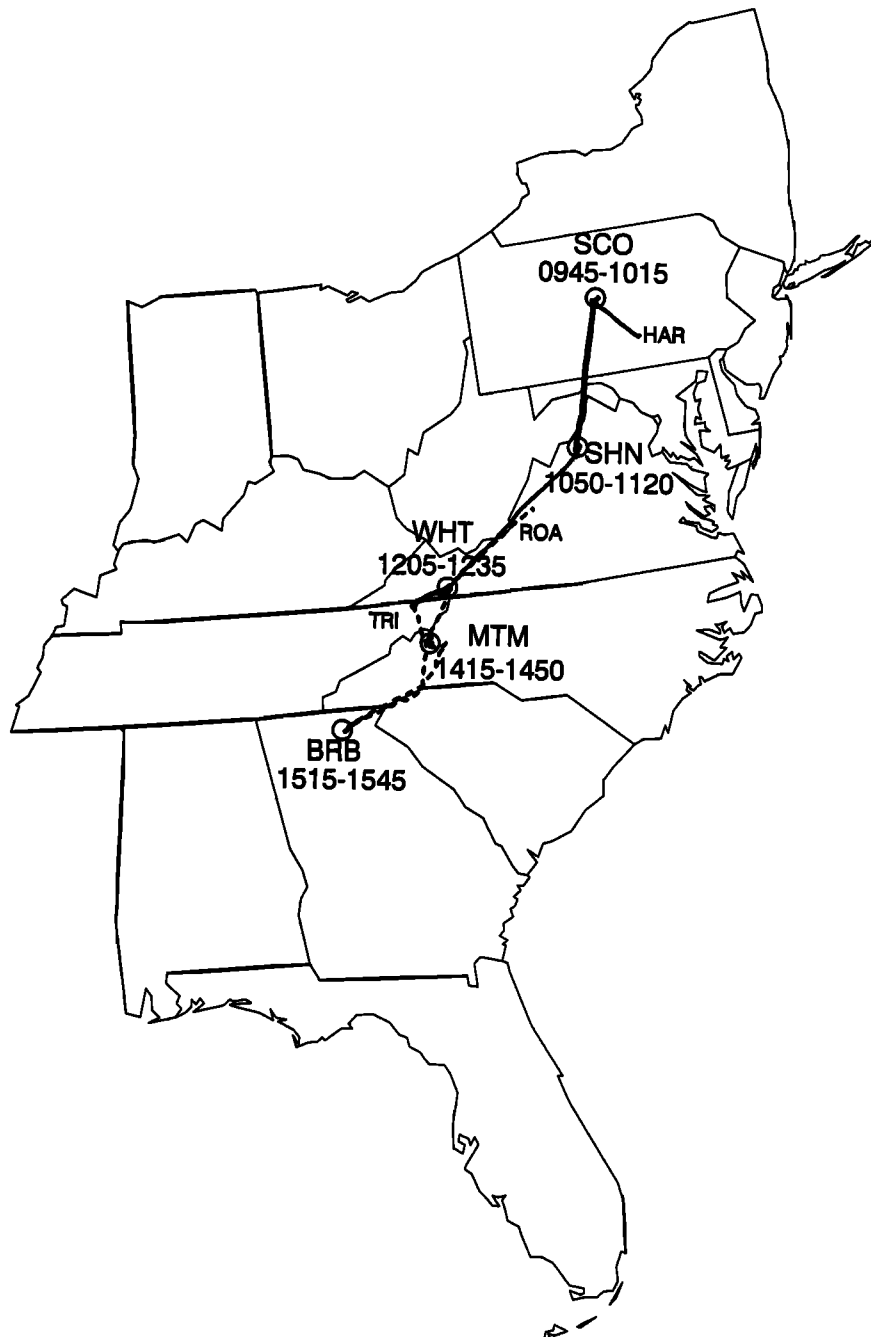


Fig. 1. Map of the eastern United States showing the flight tracks, field sites (SCO, SHN, WHT, MTM, and BRB), airports (HAR, Capitol Cities Airport, Harrisburg, Pennsylvania; TRI, Tri-Cities Airport, Tennessee; ROA, Municipal Airport, Roanoke, Virginia), and times of stepwise profiles (EST). The track of the first flight is represented by the heavy solid line, and the second by the dashed line.

minutes at each profile step over each site, the lowest of which were 270, 286, 78, 174, and 222 m above SCO, SHN, WHT, MTM, and BRB, respectively. Flight and ground sampling information from the lowest step above the site, and in two cases at an additional step below the elevation of the site, are shown in Table 1. Meteorological data are presented in Table 2. Concentration data for trace gases, except hydrocarbons, are shown in Table 3. Hourly average O_3 concentrations from

four locations in the Shenandoah National Park are listed in Table 4, and the concentrations of some hydrocarbon trace gases are listed in Table 5. Only data collected during the time of constant altitude flight were used for the aircraft-ground site comparisons. For the comparison between the aircraft and the ground values, means and standard deviations for each variable were calculated for the time period of the lowest step above each site, lasting 4 to 6

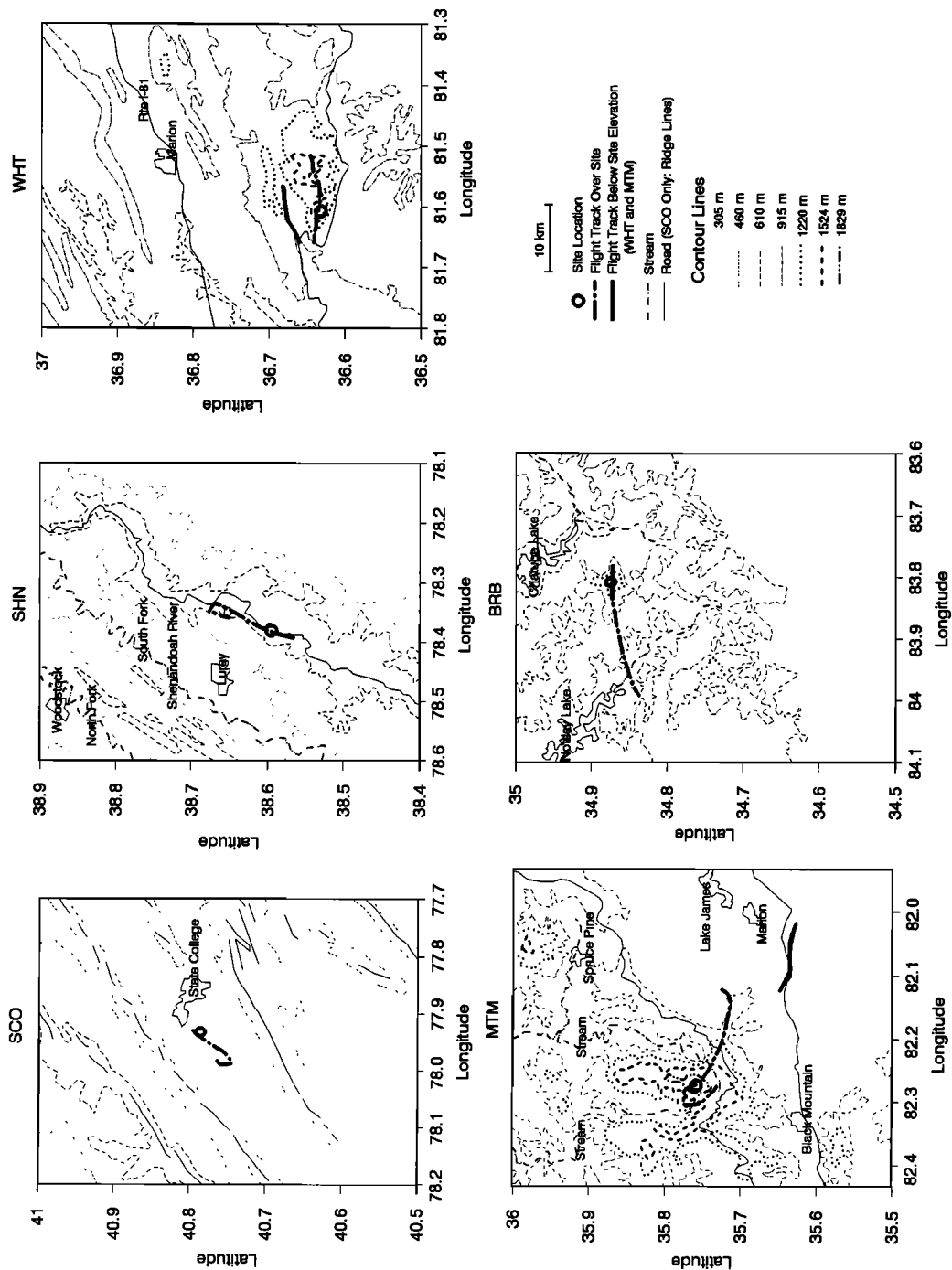


Fig. 2. Flight tracks at the lowest altitudes over the ground research sites at SCO, SHN, WHT, MTM, and BRB, and below the elevation of the ground sites at WHT and MTM, superimposed on topographic representations of the immediate vicinities.

TABLE 1. Flight and Ground Sampling Information at Five Sites in the Appalachian Region, August 16, 1988

	Observation*	Site†				
		SCO	SHN	WHT	MTM	BRB
Measurement interval, EST	A	1008:10-1010:50	1106:10-1110:20	1223:00-1226:20	1433:00-1438:40	1535:30-1539:50
	A'			1228:00-1230:00	1442:20-1444:50	
	G	0945-1015	1045-1115	1215-1245	1415-1445	1515-1545
Flight path length, km	A	10.9‡	17.7‡	13.9	25.9‡	19.1
	A'			8.9	10.8	
Distance from site (min-max), km	A	0-7	0-10	0-8	0-14	0-17.5
	A'			4.5-6	17.5-27	
Aircraft pressure altitude, mb	A	946±1	876±2	827±3	784±1	851±1
	A'			873±1	851±1	
Elevation, m ASL	A	660	1300	1760	2180	1680
	A'			1460	1540	
	G	390	1014	1682	2006	1458
Aircraft altitude over site, m	A	270	286	78	174	222
	A'			-222	-466	

*A, lowest-altitude aircraft pass over the field site; A', aircraft measurement at lower altitude than site elevation, made over lower terrain north of WHT and southeast of MTM; G, ground site.

†SCO, Scotia, PA; SHN, Shenandoah National Park, VA; WHT, Whitetop Mountain, VA; MTM, Mt. Mitchell, NC; BRB, Brasstown Bald, GA.

‡ Flight track includes a 180° turn.

min. A relatively long averaging time of 30 minutes for the ground sites was deemed necessary because the sampling scale on the ground is much longer as a result of the differences between wind speed ($2\text{--}5\text{ m s}^{-1}$) and aircraft velocity (60 m s^{-1}). Thus, the surface equivalent averaging time should be an order of magnitude longer than for the aircraft.

3. Meteorology

On August 16, 1988, a low-pressure system was located over northeastern Canada and a cold front extended from the northeastern U.S. coastline to southern Virginia. The front was found to be stationary through southern West Virginia and Ohio (Figure 3). To the north of the front, surface dew points were about 15°C ; to the south they were near 20°C . Winds south of the front were light and variable, becoming predominantly easterly late in the day. Isobaric air mass back trajectories were calculated at the surface, 850, and 700 mbar, using the method of Harris [1982]. These trajectories (shown in Figure 3) indicated that the airflows at sites south of the front were from the southeast, while those north of the front were primarily from the

north or northwest. In the vicinity of the front a transition zone was identified, where the surface flows (below the frontal boundary) were from the southeast, while the flows aloft (above the frontal boundary) were from the northwest.

On the first flight, during the portion from HAR to SCO and SHN, the skies were clear in the cooler, drier air behind the front. Significant cloudiness was detected on a portion of the flight leg between SHN and WHT as the aircraft penetrated the front, and a rain shower was experienced at the WHT site just before the airplane arrived. From WHT (i.e., about noon) to BRB and on the return as far as MTM, considerable intermittent cloudiness and numerous rain showers were observed in the warm-sector air ahead of the front. During the time that elapsed between the southward and return flight legs, the front moved southeastward, and from MTM to the refueling location at ROA the atmosphere was essentially cloud free.

4. Results

Two-dimensional plots of potential temperature (θ) and water mixing ratios (WMR) are shown in Figures 4 and 5. Similar plots for O_3 ,

TABLE 2. Meteorological Observations at Five Sites in the Appalachian Region, August 16, 1988

	Observation*	Site†				
		SCO	SHN	WHT	MTM	BRB
Wind speed, m s ⁻¹	A	9.0±3.6	7.1±2.0	9.5±3.8	9.2±3.4	5.8±1.5
	A'			4.2±2.5	6.9±3.1	
	G	1.9±0.7	4.2±0.1	4.0±0.5	3.1±2.7	4.6±1.1
Wind direction, degrees	A	319±24	282±24	335±24	21±12	104±19
	A'			350±12	262±125	
	G	330±110	295±10	333±10	102±37	245±50
Temperature, °C	A	22.8±0.2	19.3±0.2	19.3±0.4	16.1±0.2	20.9±0.2
	A'			22.7±0.2	21.4±0.2	
	G	27±1	24±1	22±1	19±2	24
Dew point, °C	A	8.0±0.5	10.3±0.5	13.3±1.2	11.1±1.0	13.1±0.8
	A'			16.8±0.3	16.4±0.5	
	G	11±1	15±1	18±2	15±1	14

Values shown are mean plus or minus standard deviation.

*A, lowest-altitude aircraft pass over the field site; A', aircraft measurement at lower altitude than site elevation, made over lower terrain north of WHT and southeast of MTM; G, ground site.

†SCO, Scotia, PA; SHN, Shenandoah National Park, VA; WHT, Whitetop Mountain, VA; MTM, Mt. Mitchell, NC; BRB, Brasstown Bald, GA.

TABLE 3. Trace Gas Concentrations by Continuous Analysis at Five Sites in the Appalachian Region, August 16, 1988

	Observation*	Site†				
		SCO	SHN	WHT	MTM	BRB
O ₃ , ppbv (range)	A	47±1 (46-49)	94±2 (91-99)	92±2 (88-96)	78±1 (75-79)	70±2 (67-73)
	A'			91±2 (88-94)	83±3 (79-89)	
	G	43±1	72±5	51±4	72±2	54
H ₂ O ₂ , ppbv (range)	A	0.6±0.05 (0.5-0.6)	0.7±0.1 (0.6-0.7)	0.9±0.2 (0.6-1.2)	1.6±0.1 (1.4-2.0)	2.0±0.2 (1.7-2.3)
	A'			1.0±0.2 (0.8-1.3)	2.3±0.3 (1.9-2.8)	
	G	NA	NA	0.4±0.1	0.8±0.2	NA
SO ₂ , ppbv (range)	A	4.1±1.2 (2.1-5.5)	>7.7	5.1±0.1 (4.9-5.2)	1.9±0.2 (1.6-2.1)	1.4±0.7 (1.0-2.9)
	A'			4.9±0.1 (4.8-5.1)	2.3±0.2 (2.1-2.5)	
	G	2.0±0.5	12.5±1.0	1.3±0.3	1.4±0.8	<1
NO _y , ppbv	A	3.2	6.5	6.0	4.5	3.3
	A'			6.3	5.0	
	G	3.2±1				1.4

Values shown are mean plus or minus standard deviation.

*A, lowest-altitude aircraft pass over the field site; A', aircraft measurement at lower altitude than site elevation, made over lower terrain north of WHT and southeast of MTM; G, ground site.

†SCO, Scotia, PA; SHN, Shenandoah National Park, VA; WHT, Whitetop Mountain, VA; MTM, Mt. Mitchell, NC; BRB, Brasstown Bald, GA.

TABLE 4. Hourly Average O₃ Concentrations at the Shenandoah National Park Observing Sites During Three Time Intervals, August 16, 1988

Site	Elevation, m	O ₃ Concentration, ppbv		
		1000-1100 EST	1100-1200 EST	1200-1300 EST
SH1	1014	69	79	88
SH2	716	79	88	97
SH3	524	72	84	92
Big Meadows	1067	90	99	107

At 1106-1110 EST the aircraft O₃ instrument measured 94±2 ppbv.

H₂O₂, SO₂, and NO_y are shown in Figures 6 through 9, respectively. Ground measurement data and corresponding aircraft data taken near the ground sites are presented in Tables 1 through 5.

The comparisons are based on the ground measurements for a half-hour period (representing 10-20 min before and after the flyby) that encompassed the lowest altitude aircraft pass over each station. The aircraft made measurements to the north of WHT and to the southeast of MTM that were done at lower altitudes than the ground elevation of these mountain measuring sites.

The aircraft flight track passed directly over the SHN site SH1 (elevation 1014 m) at the head of Shaver Hollow in the Shenandoah National Park, but O₃ measurements were also being made at two other sites in the Shaver Hollow watershed. Site SH1 and site SH3 (elevation 524 m) are 1.6 km apart, and site SH2 (elevation 716 m) is 1.0 km from SH1 and 0.6 km from SH3. In addition, the National Park Service operates three other sites in the Shenandoah National Park where O₃ measurements were being made. One of these, Big Meadows (elevation 1067 m) is about 12 km from the SH1 site and about 9 km from the southernmost aircraft position during its lowest-altitude measurements. The hourly average O₃ concentrations for these four sites are shown in Table 4.

5. Discussion

5.1. Time and Space Evolution of Atmospheric Trace Gas Concentrations

The frontal zone that existed on August 16 is clearly demonstrated by the higher θ values in the latitude region near WHT and ROA (Figure 4); also, the WMR values south of the frontal zone were higher (Figure 5). In agreement with the surface meteorological observations noted earlier, WMR values at flight altitude south of the frontal zone were higher by nearly 5 g kg⁻¹. This condition was observed on both the southward and northward flight legs.

The time series of O₃ measurements at SCO and SHN indicated that these sites experienced gradually increasing concentrations during the morning and early afternoon. At SCO the maximum on this day was 53 ppbv and at SHN it was 107 ppbv, both recorded in the early afternoon; during the refueling stop at TRI the O₃ concentration increased from approximately 110 ppbv at 1250 EST to ≥130 ppbv at 1405 EST. These observations are consistent with those of Meagher et al. [1987]; in an extended series of measurements at several low-elevation sites in the southeastern United States they found a pronounced diurnal O₃ cycle, with maximum concentrations during the early afternoon. Such

TABLE 5. Hydrocarbon Concentrations by Flask Analysis at Five Sites in the Appalachian Region, August 16, 1988

	Observation*	Site					Typical Clean Air Values
		SCO	SHN	WHT	MTM	BRB	
C ₂ H ₆ , pptv	A	1720	2740	2200	1610	1420	900
	G	1670	2630	2670	2120	1620	
C ₂ H ₂ , pptv	A	180	450	280	220	230	70
	G	180	430	340	310	270	
C ₃ H ₈ , pptv	A	510	1120	770	620	550	70
	G	670	1160	930	850	1000	
C ₄ H ₁₀ , pptv	A	170	740	350	290	550	20
	G	360	350	850	470	520	

*A, lowest altitude aircraft pass over the field site; G, ground site.

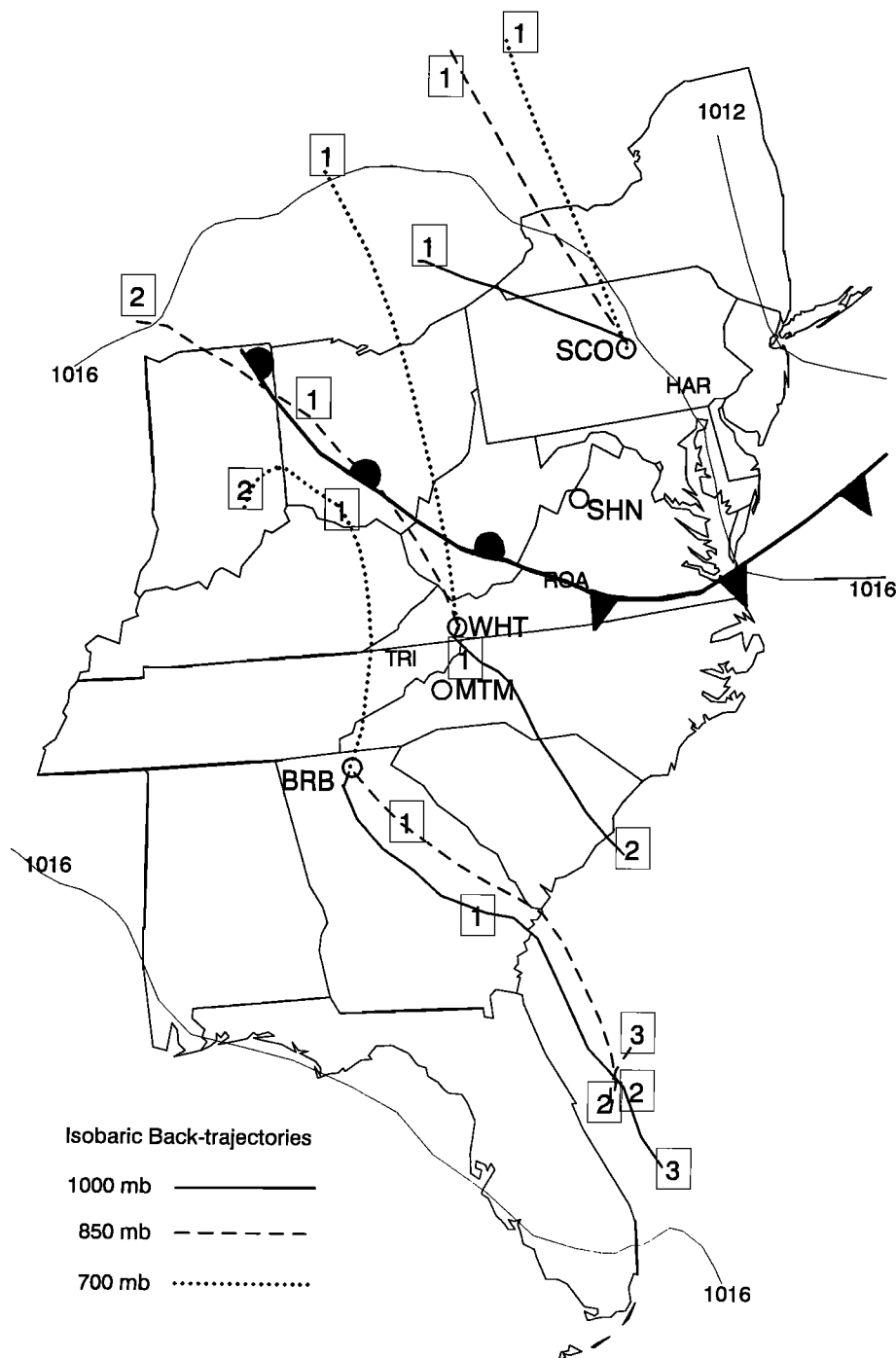


Fig. 3. Map of the eastern United States showing the locations of the field sites (small circles), the front at 0700 EST (heavy solid line with barbs), the surface pressure contours (light solid lines with pressure notations in millibars), and air mass back trajectories to end points at SCO, WHT, and BRB at 0700 EST. The air mass positions, in multiples of 24 hours before reaching the end points, are indicated by the numbers within rectangles.

a diurnal cycle was also demonstrated by Aneja et al. [1991] at a low-elevation location near the MTM site, but the high-elevation site (MTM) experienced only mild diurnal changes in which the maximum O_3 concentrations usually were recorded at night. Consistent with this observation, the O_3 concentrations at both WHT and MTM were near their lows for the 24-hour period

of August 16 at the time of the aircraft flyover; the maximum concentrations for the period were recorded several hours later.

At the beginning of the first flight (approximately 0930 EST) at HAR (Figure 6) the low-altitude O_3 concentration was less than 50 ppbv. The same low O_3 concentrations were recorded at lower altitudes over SCO.

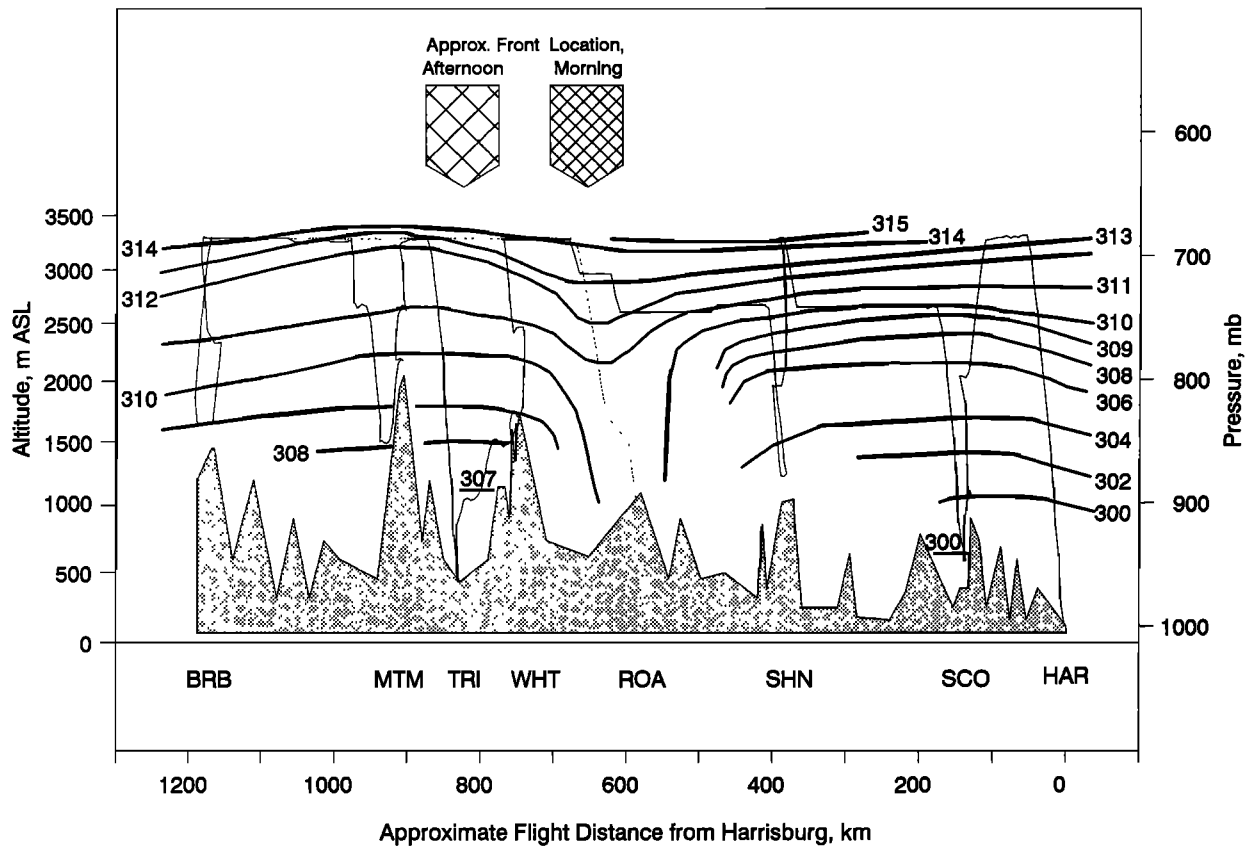
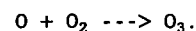


Fig. 4. Potential temperature contours (in degrees Kelvin) along the flight track, determined by atmospheric state measurements aboard the aircraft, superimposed on diagrams of the aircraft flight altitude (thin lines) and the terrain elevation along the flight track (shaded). The dashed line represents the flight profile from BRB to ROA.

Thereafter, later in the day, the highest concentrations were recorded at the lowest altitudes, which is consistent with local photochemical production. At the aircraft cruise altitudes (3–3.5 km above sea level (ASL)) greater O_3 concentrations were recorded south of the frontal boundary, particularly between MTM and BRB, than to the north of it. This zone of O_3 concentrations greater than 80 ppbv probably resulted from orographic lifting over the southeastern slope of the Blue Ridge Mountains coupled with convective activity and photochemistry, which was evidenced by the higher concentrations of NO_y ; however, the general north to south upward slope of the isopleths of all the measured trace gases is regarded as primarily a function of the daily evolution of the planetary boundary layer.

North of the frontal boundary the maximum H_2O_2 concentrations of 1.5 ppbv or slightly greater (Figure 7a) were measured at 2.5–3 km ASL. This is a region of atmospheric stability, as indicated by the closer spacing of the θ isopleths (Figure 4). This H_2O_2 maximum is consistent with the report of Ray et al. [1992] showing that H_2O_2 accumulates near the top of the boundary layer. However, it should be pointed out that O_3 levels are not elevated in this region. H_2O_2 concentrations (Figure 7) south of

the frontal region were significantly greater than those to the north, especially at low altitudes, as expected based on the higher WMR values [Atkinson and Lloyd, 1984]. Also noteworthy were the high concentrations of H_2O_2 (about 2.5 ppbv, Figure 7b) at the highest flight altitudes, in the region where orographic lifting and convective activity involving pollutants from the populated region are suspected of having produced higher O_3 concentrations. The possibility that this was what happened is further suggested by the slightly elevated concentrations of SO_2 and NO_y in this zone. H_2O_2 and O_3 are produced in the atmosphere by different mechanisms, and consequently their vertical profiles are not necessarily parallel [Ray et al., 1992; Van Valin et al., 1990]. The formation of excess O_3 (above that found in the unperturbed atmosphere) is expected to be closely related to anthropogenic activity because NO is essential to its production. The main O_3 production mechanism in the troposphere is through



NO is reoxidized by

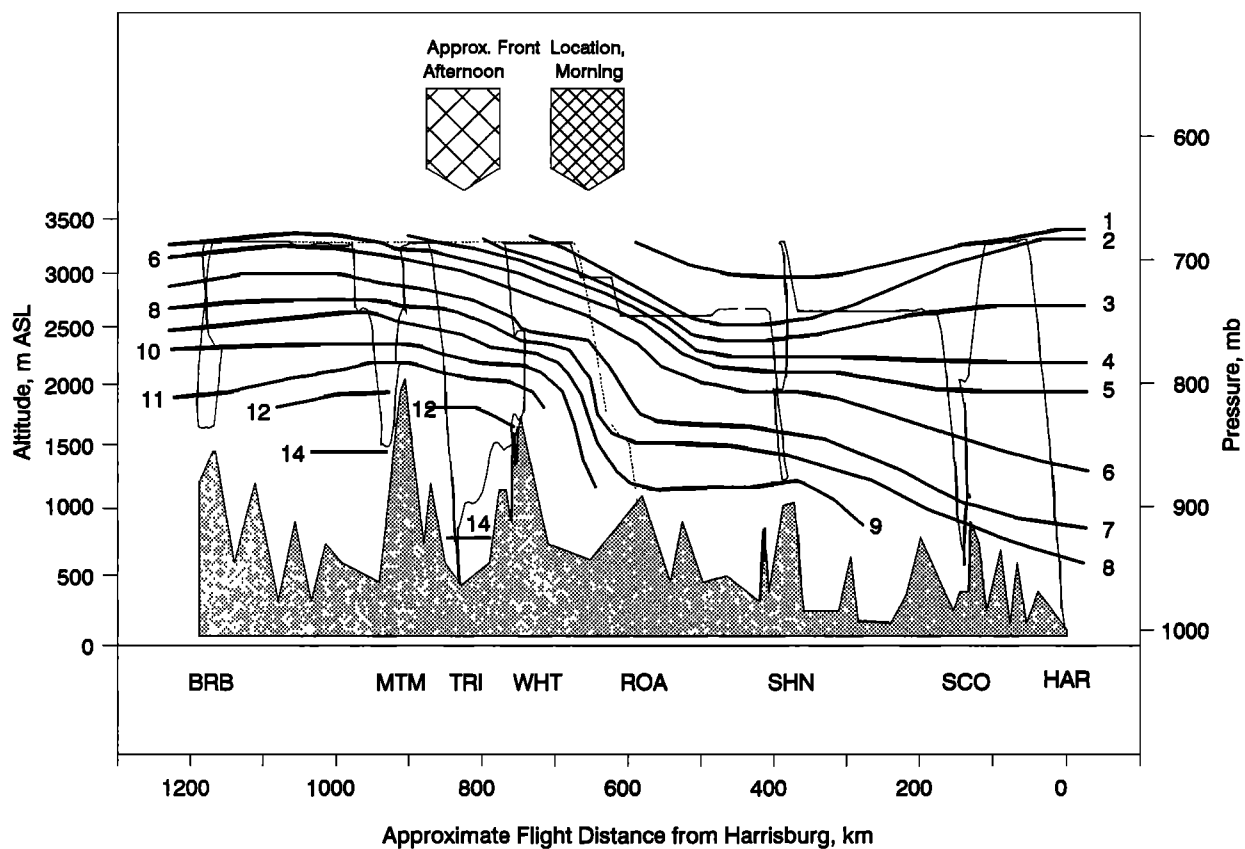


Fig. 5. Water vapor mixing ratio contours (g kg^{-1}) derived from measurements aboard the aircraft, as in Figure 4.

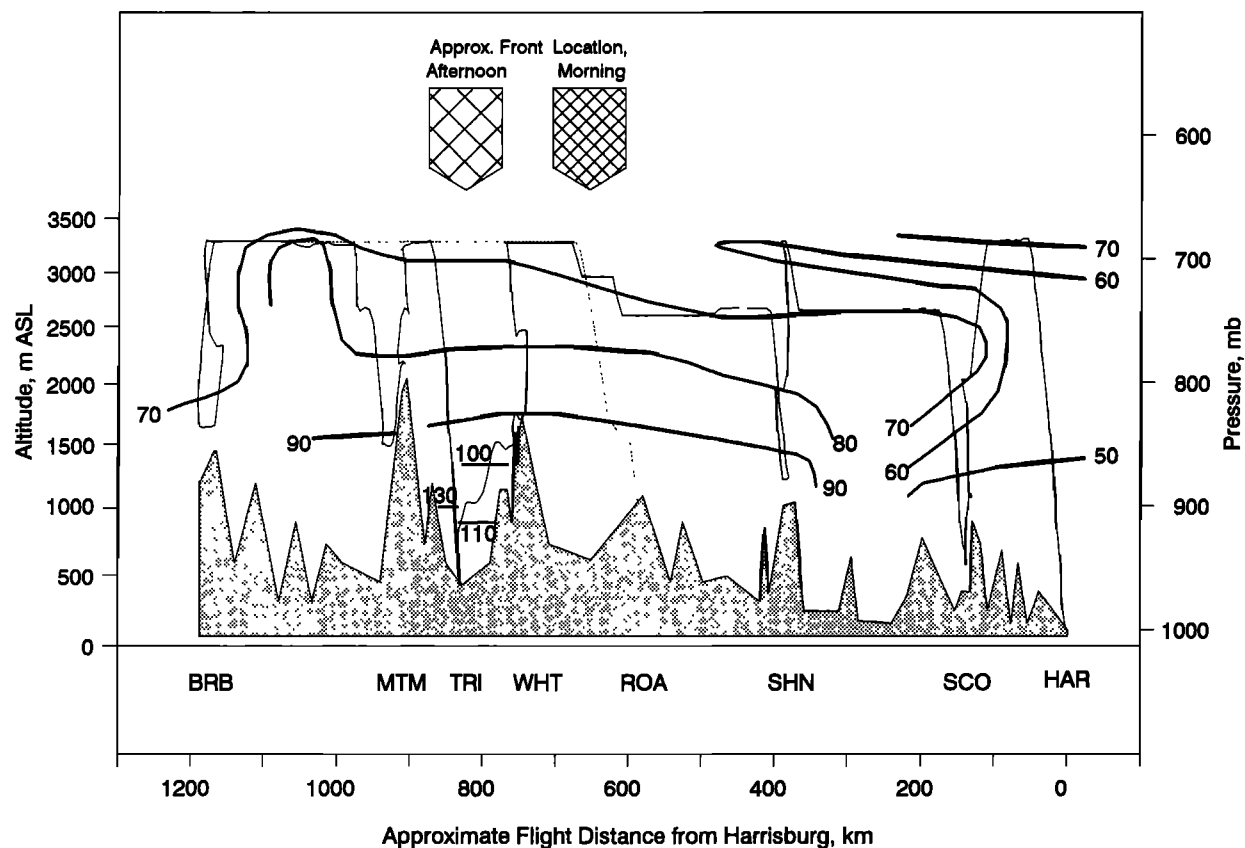


Fig. 6. Atmospheric O_3 concentration contours (ppbv) derived from measurements aboard the aircraft, as in Figure 4.

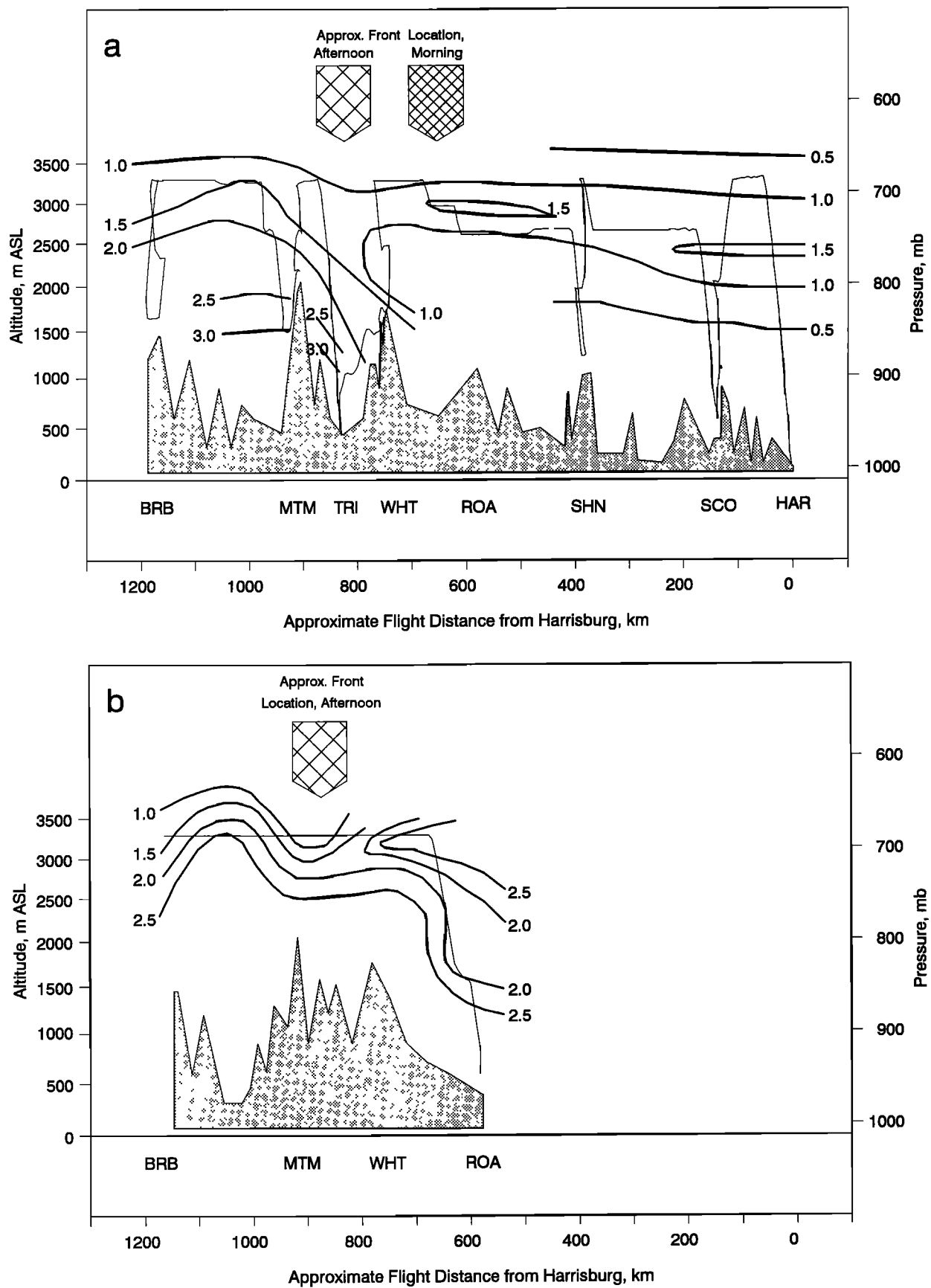


Fig. 7. Atmospheric H_2O_2 concentration contours (ppbv) derived from measurements aboard the aircraft, superimposed on diagrams of the aircraft flight altitude (thin lines) and the terrain elevation along the flight track (shaded). (a) Flights from HAR to BRB; (b) return flight from BRB to ROA.

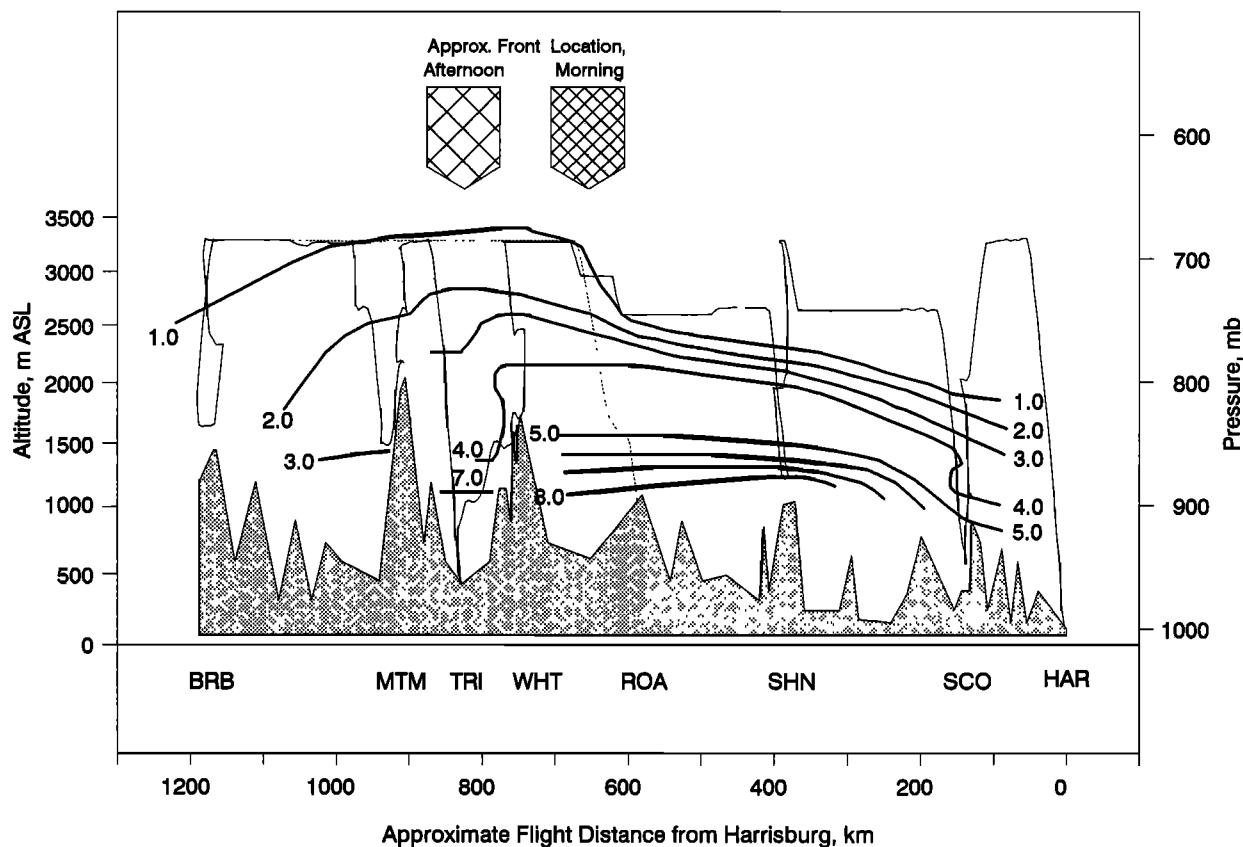
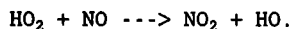
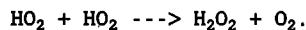


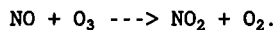
Fig. 8. Atmospheric SO_2 concentration contours (ppbv) derived from measurements aboard the aircraft, as in Figure 4.



In an NO -lean atmosphere there will be a buildup of HO_2 radicals that can promote the recombination



The latter reaction proceeds faster in the presence of water [Atkinson and Lloyd, 1984]; this reaction becomes dominant for removal of HO_2 in the NO -lean atmosphere. This above scheme oversimplifies the atmospheric process. NO under some circumstances (lack of hydrocarbons and/or solar radiation) scavenges O_3 by



Thus, there is a wide range of circumstances under which either one or both O_3 and H_2O_2 can be present in high, or low, concentrations. One process by which H_2O_2 is removed from the atmosphere is solution in cloud water; therefore, the intermittent cloudiness encountered at cruise altitude during the flight to BRB and return as far as MTM would be expected to inhibit the buildup of H_2O_2 . Between MTM and ROA the absence of clouds could have permitted accumulation of H_2O_2 to the highest concentrations observed at this altitude (Figure 7b).

Higher pollution levels were noted north of the front at low altitudes; however, a rapid decrease with increasing altitude was also

measured there, due to atmospheric stability. In the southern region, significant pollution levels (>1.0 ppbv) of SO_2 and NO_y were measured even at the highest flight altitudes (Figures 8 and 9). It is likely that these levels of SO_2 and NO_y were to some extent related to vertical transport through orographic lifting and convective activity, but the observed concentrations at cruise altitude were more uniformly distributed through the southern sector than were O_3 and H_2O_2 concentrations. This suggests that part of the SO_2 and NO_y present at this altitude was transported from a more distant source region. The air mass back trajectories ending at WHT and BRB, indicated in Figure 3, suggest the Midwest industrialized region as a probable source. It is noteworthy that the contours of SO_2 and NO_y are similar but not identical, which suggests that the major regional pollution sources are stationary and emit both substances, rather than automotive, which is nearly exclusively a source of NO_y .

5.2 Relationship Between the Ground and Aircraft Data

An examination of the data presented in Tables 2 and 3 indicates that there is not a consistent or close agreement between the measurements aloft and on the ground. The closest agreement was found for the SCO site. At an altitude of 270 m above the site the

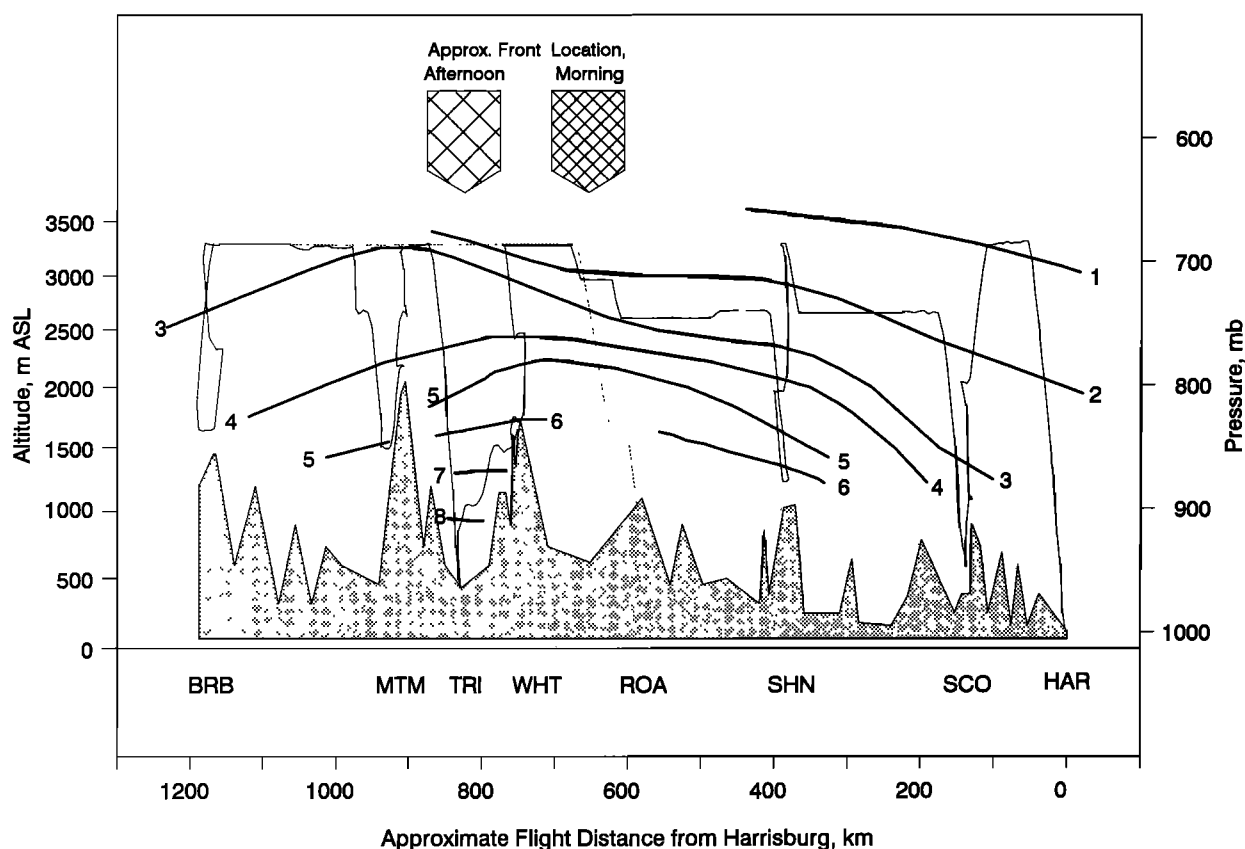


Fig. 9. Atmospheric NO_x concentration contours (ppbv) derived from measurements aboard the aircraft, as in Figure 4.

temperature and dew point were 5°C and 3°C lower, respectively, than at the surface. These differences are consistent with ground values in view of the measured atmospheric lapse rates. Wind speed at the 270 m altitude was several times greater than at the surface. At the SCO site, which is situated in relatively level terrain (Figure 2), the agreement between the aircraft and surface gas analyses was reasonably good (Table 3 and Van Valin et al. [1991]); that is, extrapolation of the stepwise profile values to the ground produced agreement within the limits of experimental uncertainty.

Even though the atmosphere at SHN was relatively free of obvious convective activity there was more atmospheric mixing than at SCO, but the agreement between aircraft and ground data was better at SCO than at SHN. The agreement was further degraded at WHT, although active convective mixing of the atmosphere was in progress, and there had been a rain shower immediately prior to the aircraft flyby. At the latter site the secondary pollutant concentrations at ground level were much lower than those observed with the aircraft. While the ground-level concentration of the O_3 was typical of clean (or at most, mildly polluted) air conditions ($\text{O}_3 = 51$ ppbv), the atmospheric concentrations measured on the lowest altitude flight legs were indicative of a regionally polluted atmosphere ($\text{O}_3 = 91$ ppbv). This situation of poorer agreement between the aircraft and ground measurements in regions of

greater atmospheric mixing is counter to the logical expectation of a positive, not negative, relationship. The deterioration of aircraft-ground agreement as atmospheric mixing increased suggests the existence of other variables that can only be guessed, such as increased dry deposition under the influence of sunlight and a degree of decoupling of the planetary boundary layer from the air actually in contact with vegetation and the Earth's surface. The fact that the concentration of O_3 at SHN, and of both O_3 and H_2O_2 at WHT, increased for a few hours after completion of the aircraft flyby to levels comparable with those observed by the aircraft seems to suggest that involvement of the very-near-surface atmospheric layer proceeds more slowly than does the mixing of the wider atmosphere.

The wind direction measurements at the surface and aboard the aircraft were in close agreement at SCO, SHN, and WHT (Table 1), but upslope airflow observed during the afternoon on the western slope of Brasstown Bald caused west-southwest flows near the surface, while the aircraft measured east-southeast wind in the free atmosphere. The cause of the wind direction discrepancies at MTM is less clear, although the presence of convective activity, including rain showers, suggests that local winds, especially near the surface, would be quite variable.

These data, therefore, suggest that the aircraft-measured values at roughly 250 m above the site represented different conditions than

those measured at the ground. This hypothesis can be supported from the differences observed in the atmospheric state measurements. Although excellent agreement between aircraft and BAO measurements was found when the flyby intercomparison was done prior to the flights in the Appalachian region, the aircraft measurements versus those at the ground sites in the Appalachian region were outside the limits of reasonable agreement. This condition can be further demonstrated when the data collected at altitudes below the elevations of the ground sites are considered. At the two most mountainous sites, WHT and MTM, where this was done (Figure 2), the meteorological and gas analysis data from the lower altitude traverses were closer to those from the higher altitude traverses than to the ground site data (Tables 2 and 3). The fact that only after 1-3 hours were the data at WHT more consistent with the aircraft data suggests that the stirring from convective activity did not involve near-surface air for some time. Although the true microstate of the atmosphere is unknown, these observations seem to indicate that the atmosphere on a very small vertical scale, i.e., on the canopy scale, was separate from the well-mixed boundary layer. This is also consistent with the observation that it took a few hours for the very near-surface air to come into equilibrium with the upper layers. As atmospheric mixing progressed in the afternoon hours these differences seemed to diminish.

An example of midday atmospheric variability is provided by the various ground stations within a small area at SHN. At 1300 EST the hourly average O_3 concentrations recorded at these various sites (Table 4) differed by as much as 19 ppbv, but all exhibited similar patterns, which involved strong increases in O_3 concentrations from early morning until about 1300 EST, followed by sharp decreases until about 1600 EST. The difference between the highest and lowest concentrations of O_3 in the 3-hour period (1000-1300 EST) in the SHN area, 38 ppbv, is far greater than the 23-ppbv difference found between the aircraft and the SH1 site. To the extent that the aircraft-measured O_3 concentrations can be compared with the hourly averaged data from the Big Meadows site, which is a predominantly open, grassy area, the agreement is excellent (94 ± 2 ppbv aircraft at 1106-1110 EST versus 90 ppbv average from 1000 to 1100 EST and 99 ppbv from 1100 to 1200 EST; see Table 4). The Big Meadows measurements were taken at 4 m above the ground, compared with a sampling height of 3 m within the forest canopy at the other SHN sites. Gilliam et al. [1989] and Poulida et al. [1991] have argued that O_3 is significantly reduced by deposition to vegetation, particularly to deciduous leaves, thus making O_3 concentrations in the forest lower than in adjacent, open areas. That the aircraft-measured concentrations of O_3 above all stations (and for this discussion, H_2O_2 as well) were greater than the ground values is expected because these secondary pollutants are generated aloft and diffuse to the surface, where they are removed primarily by dry deposition. For three of the sites, WHT, MTM, and BRB, the same point could be made regarding SO_2 and NO_y . Since these sites are removed from pollution sources, pollutant transport to the site would be in the free atmosphere with diffusion downward to the surface.

5.3. Hydrocarbon Concentrations

As shown in Table 5, air at all of the sites contained elevated levels of the four hydrocarbons, C_2H_6 , C_2H_2 , C_3H_8 , and $n-C_4H_{10}$, relative to typical clean air [Blake et al., 1992]. The lifetimes of these substances in the atmosphere are relatively long (on the order of weeks); therefore, transport from distant regions is an important factor in their atmospheric concentrations. As can be seen from the air mass back-trajectories of Figure 3 and the data in Table 5, there is a consistency between atmospheric transport path and hydrocarbon concentrations. The air masses sampled at some sites passed over highly industrialized areas (SHN and WHT) and some were from rural areas (MTM and BRB) or where the air mass being sampled passed quickly over industrial zones (SCO).

Two of the hydrocarbons, C_3H_8 and $n-C_4H_{10}$, are the primary constituents of liquid petroleum gas (LPG) that is widely used in rural areas; in some cases leakage from LPG tanks is significant. LPG from different vendors can have widely varying ratios of C_3H_8 and $n-C_4H_{10}$, so little can be expected regarding the apparent lack of correlation between these two substances in the aircraft versus the ground samples, where significant local influence was probable. The other two hydrocarbons, C_2H_2 and C_2H_6 , are less likely to have major local point sources, therefore, they represent regional pollution levels. That is probably why the variation between ground and aircraft samples, and to a certain extent between the sites, is smaller.

6. Conclusions

The results of the comparison between the aircraft and ground-based atmospheric measurements reveal that under the atmospheric conditions prevailing on the day of the flights from HAR to BRB, the disagreement exceeded the limits of experimental error. The conclusion was based on measurements of state parameters for which the uncertainty is small, and is supported by the measurements of the atmospheric pollutant species. This suggests that measurements at these rugged surface sites may not represent the planetary boundary layer for certain periods of time, such as the time of the present study.

Acknowledgments. We thank D. Parrish, Aeronomy Laboratory, NOAA, for making the SCO surface measurements available to us, and J. Meagher and K. Olszyna, Air Quality Branch, Office of Natural Resources and Regional Development, Tennessee Valley Authority, for making the WHT surface measurements available to us. J. M. Harris, Climate Monitoring and Diagnostics Laboratory, NOAA, performed the air mass back-trajectory calculations. We appreciate the professionalism and dedication of the pilots, T. Gates and R. Morris.

References

- Aneja, V. P., S. Businger, Z. Li, C. S. Claiborn, and A. Murthy, Ozone climatology at high elevations in the southern Appalachians, *J. Geophys. Res.*, **96**, 1007-1021, 1991.
- Atkinson, R., and A. Lloyd, Evaluation of kinetic and mechanism data for modeling of

- photochemical smog, J. Phys. Chem. Ref. Data, **13**, 315-444, 1984.
- Blake, D. R., D. F. Hurst, T. W. Smith, Jr., W. J. Whipple, T.-Y. Chen, N. J. Blake, and F. S. Rowland, Summertime measurements of selected nonmethane hydrocarbons in the Arctic and Subarctic during the 1988 Arctic Boundary Layer Expedition (ABLE3A), J. Geophys. Res., **97**, 16,559-16,588, 1992.
- Boatman, J. F., D. L. Wellman, R. C. Schnell, K. M. Busness, M. Luria, and C. C. Van Valin, In-flight intercomparison of some aircraft meteorological and chemical measurement techniques, Global Biogeochem. Cycles, **2**, 1-11, 1988.
- Boatman, J. F., D. L. Wellman, C. C. Van Valin, R. L. Gunter, J. D. Ray, H. Sievering, Y. Kim, S. W. Wilkison, and M. Luria, Airborne sampling of selected trace chemicals above the central United States, J. Geophys. Res., **94**, 5081-5093, 1989.
- Boatman, J. F., N. Laulainen, J. Ray, C. Van Valin, L. Gunter, R. Lee, D. Luecken, and K. Busness, Acid precursor concentrations above the northeastern United States during summer, 1987: Three case studies, J. Geophys. Res., **95**, 11,831-11,845, 1990.
- Dickerson, R. R., A. C. Delany, and A. F. Wartburg, Further modifications of a commercial NO_x detector for high sensitivity, Rev. Sci. Instrum., **55**, 1995-1998, 1984.
- Gilliam, F. S., J. T. Sigmon, M. A. Reiter, and D. O. Krovetz, Elevational and spatial variation in daytime ozone concentrations in the Virginia Blue Ridge Mountains: Implications for forest exposure, Can. J. For. Res., **19**, 422-426, 1989.
- Gotaas, Y., OECD program on long range transport of air pollutants-measurements from aircraft, Aerosols: Anthropogenic and Natural, Sources and Transport, Ann. N. Y. Acad. Sci., **338**, 453-462, 1980.
- Harris, J. M., The GMCC atmospheric trajectory program, NOAA Tech. Memo. ERL ARL-116, 30 pp., NOAA Air Resour. Lab., Rockville, Md., 1982.
- Harrison, R. M., C. D. Holman, H. A. McCartney, and J. F. R. McIlveen, Nocturnal depletion of photochemical ozone at a rural site, Atmos. Environ., **12**, 2021-2026, 1978.
- Lazrus, A. L., G. L. Kok, J. A. Lind, S. N. Gitlin, B. G. Heikes, and R. E. Shetter, Automated fluorometric technique for hydrogen peroxide vapor in air, Anal. Chem., **58**, 5594-5597, 1986.
- Meagher, J. F., N. T. Lee, R. J. Valente, and W. J. Parkhurst, Rural ozone in the southeastern United States, Atmos. Environ., **21**, 605-615, 1987.
- Possiel, N. C., C. W. Spicer, P. R. Sticksel, G. M. Sverdrup, A. J. Alkezweeney, and W. E. Davis, Northeast corridor regional modeling project: Ozone and precursor transport in New York City and Boston during the 1980 field program, EPA-450/4-84-011, 64 pp., EPA Office of Air Quality Planning and Standards, Research Triangle Park, N. C., 1984.
- Poulida, O., R. R. Dickerson, B. G. Doddridge, and J. Z. Holland, Trace gas concentrations and meteorology in rural Virginia, 1, Ozone and carbon monoxide, J. Geophys. Res., **96**, 22,461-22,475, 1991.
- Ray, J. D., C. C. Van Valin, and J. F. Boatman, The vertical distribution of atmospheric H₂O₂: A case study, J. Geophys. Res., **97**, 2507-2517, 1992.
- Tommerdahl, J. B., J. H. White, R. B. Strong, J. E. Sickles, M. L. Saeger, and J. J. B. Worth, Aircraft measurements of pollutants and meteorological parameters during the sulfate regional experiment (SURE) program, EA-1912, Res. Proj. 862-4, Elec. Power Res. Inst., Palo Alto, Calif., 1981.
- Van Valin, C. C., M. Luria, J. D. Ray, and J. F. Boatman, Hydrogen peroxide and ozone over the northeastern United States in June 1987, J. Geophys. Res., **95**, 5689-5695, 1990.
- Van Valin, C. C., M. Luria, J. D. Ray, and J. F. Boatman, A comparison of surface and airborne trace gas measurements at a rural Pennsylvania site, J. Geophys. Res., **96**, 20,745-20,754, 1991.

V. P. Aneja, Department of Marine, Earth, and Atmospheric Sciences, North Carolina State University, Raleigh, NC 27695

D. R. Blake, Department of Chemistry, University of California, Irvine, CA 92717

J. F. Boatman, M. Luria, and C. C. Van Valin, NOAA Air Resources Laboratory, Aerosol Research Section, 325 Broadway, Boulder, CO 80303

M. Rodgers, School of Geophysical Sciences, Georgia Institute of Technology, Atlanta, GA 30332

J. S. Sigmon, School of the Environment, Duke University, Chapel Hill, NC 27708

(Received August 22, 1992; revised August 27, 1993; accepted September 16, 1993.)